

Potentiometric Nonaqueous Titration of Substituted Fatty Acids

JACK RADELL and E. T. DONAHUE

Eastern Regional Research Laboratory, Philadelphia 18, Pa.

IN THE course of a study of wool wax fatty acids, it was found that these mixed acids could not be titrated satisfactorily in 95% ethyl alcohol with 0.1N aqueous sodium hydroxide and phenolphthalein indicator. The difficulty was the result of the fact that highly colored samples obscured the end point, and even with the less highly colored samples a gradual change of indicator color occurred, making the end point difficult to determine. Attempts to circumvent these difficulties by using glass and calomel electrodes with a Beckman Model H-2 pH meter, produced curves that did not have a steep enough slope at the equivalence point to give accurate results. Consequently, the method of nonaqueous potentiometric titration was investigated. The feasibility of titrating fatty acids in nonaqueous solvents has been indicated in the literature (1, 2, 5).

Essentially, the method used in this paper has been described by Fritz and Lisicki (3). Some simplifying modifications have been introduced, and the method has been extended to the titration of substituted fatty acids.

EXPERIMENTAL

REAGENTS AND APPARATUS. Methanol, ACS reagent grade. Benzene, ACS reagent grade. Solvent, benzene-methanol (3 to 1 by volume). Sodium methoxide, 95% or better. Benzoic acid, National Bureau of Standards, primary standard. Lithium chloride, ACS reagent grade. Beckman pH meter, Model H-2. Electrodes, calomel and antimony.

Titration flask, modified iodine flask for potentiometric titrations (4).

Buret, 10 ml., graduated to 0.05 ml.

SODIUM METHOXIDE SOLUTION. To prepare an approximately 0.1N solution, about 6 grams of sodium methoxide, 103 ml. of methanol, and 615 ml. of benzene are put in a 1-liter Erlenmeyer flask, the flask is stoppered, and the solution is stirred with a magnetic stirrer for 15 minutes. A large quantity of undissolved sodium methoxide indicates that it has deteriorated excessively and fresh material should be used. The solution, if necessary, is filtered and stored in a glass-stoppered borosilicate glass bottle. It is necessary to keep the sodium methoxide and the sodium methoxide solution in stoppered flasks. No precautions are necessary to prevent the stopper from sticking. A solution of sodium methoxide showed little change in normality over a period of 6 months. The solution need not be restandardized more often than once a week.

PROCEDURE

The acid sample or the standard benzoic acid is weighed into a tared 250-ml. titration flask (4). The sample size should be chosen so that about 7 ml. of 0.1N sodium methoxide solution are required. About 0.2 gram of lithium chloride and 50 ml. of the benzene-methanol solvent are added. The flask is stoppered and the contents are allowed to go into solution (10 to 15 minutes). A glass or Teflon-encased stirrer is introduced, and the electrodes, previously soaked for 0.5 hour in the benzene-methanol solvent, are inserted into the side arms of the flask. The antimony electrode is inserted into the electrode jack normally used for the calomel electrode, and the calomel electrode is adapted to fit the other jack by means of a terminal connector. The solution in the titration flask is stirred by the magnetic stirrer and titrated at a reasonably uniform rate. At first, readings are taken at every 0.5 ml., but at every 0.1 ml. near the equivalence point.

Attempts to avoid plotting each titration by titrating to a fixed millivoltage reading proved impractical because of the difficulty of reproducing conditions. Erratic behavior of the meter needle, which may be caused by several factors, may be eliminated by permitting a 0.5-hour warm-up period for the pH meter,

by reversing the plug in the receptacle, or occasionally by adding a milliliter of methanol to the solution being titrated.

RESULTS

Results of the titrations are listed in Table I. Characteristic titration curves are shown in Figure 1, in which the volume of titrant is plotted against millivoltage readings. Titration of the benzene-methanol solvent with lithium chloride added indicated no alkali was consumed by these reagents.

There is reason to believe that some of the hydroxy acids present in wool wax acids may be lactonized, but a sample of γ -stearylactone gave a blank titration.

The titration curve for α -sulfolpalmitic acid and ammonium α -sulfolpalmitic acid in Figure 1 showed the presence of two breaks. The first break, unlike the second, was not pronounced

Table I. Determination of Neutralization Equivalents

Acid	Theory	NaOMe Found	0.1N NaOH Found ^a
Stearic	284.5	285	284.2
α -Bromopalmitic	335.3	337	336.5
α -Sulfolpalmitic	168.2	171	170.7
Ammonium α -sulfolpalmitic	176.7	184	182.6
9,10-Dihydroxystearic	316.5	312	315.4
9,10-Epoxyoctadecaric	298.5	303	298.7
12-Ketostearic	298.5	296	294.0
Mixed aminostearic	299.9	293	296.8
Mixed wool wax	...	384	372
γ -Stearylactone	No reaction	No reaction	No reaction
ϵ -Caprolactam	No reaction	No reaction	No reaction

^a This determination was made with 0.1N sodium hydroxide, 95% ethyl alcohol solvent, and a phenolphthalein indicator.

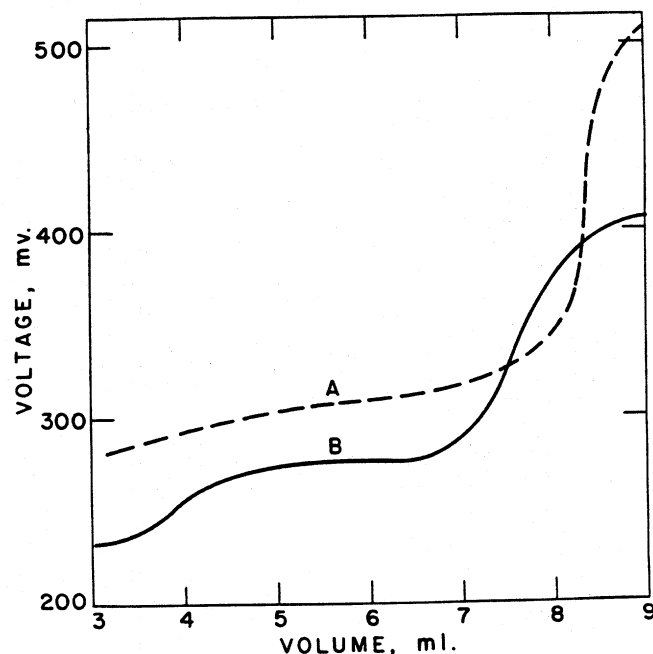


Figure 1. Titration of Wool Wax Acids and Substituted Fatty Acids

- A. Representative curve for wool wax, α -bromopalmitic; 9,10-dihydroxystearic; 9,10-epoxyoctadecaric, 12-ketostearic, and mixed aminostearic acids
- B. Representative curve for α -sulfolpalmitic and ammonium α -sulfolpalmitic acids

enough to obtain an accurate end point. Attempts to titrate α -mercaptopalmitic acid were unsuccessful.

DISCUSSION

Application of the potentiometric nonaqueous titration method to mixed wool wax acids has made possible the determination of neutralization equivalents, which usually were unattainable or grossly inaccurate. The relatively pure and colorless model compounds listed in Table I demonstrate the comparable accuracy of the nonaqueous methods and the accepted method for the determination of neutralization equivalents. The mixed wool wax acid sample which gave the best agreement by the two methods is given in Table I. Other mixed wool wax acid samples gave either poorer agreement between the two methods or could be titrated only by the nonaqueous method.

The compounds used demonstrate the feasibility of titrating fatty acids containing substituted bromine or an amino, epoxy, dihydroxy, α -sulfonic acid, and ammonium α -sulfonate group. This work has indicated that lactone, lactam, and epoxy functional groups do not interfere in the determination of the neutralization equivalent. This method has also been used to analyze samples derived from wool wax which have an acid number as low as 17 and are so highly colored that they could not be analyzed by the indicator method.

Determination of aminostearic acid (mixed position isomers) dissolved in 95% ethyl alcohol and titrated potentiometrically

with 0.1N aqueous sodium hydroxide was unsuccessful unless the amino group was first allowed to react with formaldehyde. In the method here employed, the methoxide ion is capable of titrating the aminostearic acid directly.

Similarly, the ammonium α -sulfopalmitic acid which resulted in appreciable precipitate and a gradual color change when titrated with 0.1N aqueous sodium hydroxide in 95% ethyl alcohol could be readily titrated potentiometrically with sodium methoxide in the benzene-methanol solvent.

ACKNOWLEDGMENT

The samples of α -bromopalmitic, α -sulfopalmitic, and ammonium α -sulfopalmitic acids were kindly supplied by J. K. Weil. The 9,10-dihydroxystearic, 9,10-epoxystearic, 12-ketostearic acids; and mixed aminostearic acids were supplied by Daniel Swern and the γ -stearolactone by Abner Eisner, all members of the laboratory staff.

LITERATURE CITED

- (1) Folin, O., and Flanders, F. F., *J. Am. Chem. Soc.*, **34**, 774 (1912).
- (2) Folin, O., and Wentworth, A. H., *J. Biol. Chem.*, **7**, 421 (1910).
- (3) Fritz, J. S., and Lisicki, N. M., *ANAL. CHEM.*, **23**, 589 (1951).
- (4) Ogg, C. L., Porter, W. L., and Willits, C. O., *IND. ENG. CHEM., ANAL. ED.*, **17**, 394 (1945).
- (5) Rescorla, A. R., Carnahan, F. L., and Fenske, M. R., *Ibid.*, **9**, 505 (1937).